

BIOMATERIALS

UDC 666.1-405.8

GLASS-BASED POROUS MATERIALS

P. D. Sarkisov,¹ E. E. Stroganova,¹ N. Yu. Mikhailenko,¹ and N. V. Buchilin¹

Translated from *Steklo i Keramika*, No. 10, pp. 13 – 16, October, 2008.

The basic methods of manufacturing porous glass and glass-ceramic materials were examined and analyzed on the example of bioactive materials for bone endoprosthesis. The possibility of using sol-gel technology for forming porous structures with the 3D model developed was demonstrated.

Inorganic porous materials such as foam concrete, foam glass, and claydite are widely used for fabricating load-bearing structures, heat and sound insulating panels, and heat-saving elements due to the macroporous structure with pores larger than 1 mm. Ceramic materials that have high resistance to different aggressive media and a microporous structure, with a pore size range from several micrometers to 1 mm, are frequently used for filtering and catalytic systems. The pore sizes in polymeric, ceramic, and glass molecular sieves, membranes, and filters for separation of biological systems are comparable to the size of cells and proteins. Macro- and microporous materials are obtained with the well-known and well developed methods of sintering, foaming, or duplication, while nanoporous materials usually require development of new, original manufacturing methods [1].

The new approaches to fabricating materials with a defined pore structure and porosity type can be traced on the example of bioactive materials for bone endoprosthesis based on calcium phosphates and silicate and phosphate glasses. The analysis and generalization of world advances in creating and using new medical implant materials indicates their broad possibilities and prospects for development. According to the estimations of experts, more than 600,000 bone operations are performed in the world: up to 300,000 in the US and more than 100,000 in Russia. The overall market for biomaterials in the leading countries of the world is estimated as follows (2003 data): USA — \$1.16 billion; Japan — \$430 million; Europe — \$230 million. The predicted increase in this sector is a minimum of 20% a year.

The last generation of biomaterials for bone endoprosthesis — the “truly intellectual” generation [2] — is manufactured by growing living cells of a certain type on a biomaterial substrate and then introducing them in the body as a unified cell-biomaterial structure. The role of the support is played by bioactive ceramic, glass, glass-ceramic, or composite materials whose structure is formed so that the cells required for formation of some type of tissue can penetrate, be attached, and grow in contact with the tissues in the living medium. The structure of the biomaterial means the level and character of the porosity and the pore shape and size. Penetration of bone cells in the support is only possible when the pores are a minimum of 150 μm in size, and the pores must be open and approximately 500 μm in diameter for formation of a vascular system that will maintain the vital activity of these cells in the implant.

The currently most common methods of fabricating glass, glass-ceramic, and composite porous materials are shown in Fig. 1. The methods traditional in glass technology (etching of the soluble constituent of liquating glass fibers and foaming of a viscous glass melt) are based on the structural features of liquating glasses and sitalls and the viscosity parameters of the glass melts.

When the first method is used, nano- and microporous materials are obtained, and with the second method, macroporous materials with branched open pores are obtained. The number and size of the pores in the first case are a function of the completeness of phase separation and the ratio of soluble and insoluble phases in the structure of the glass or glass-ceramic material and the kinetic parameters of the dissolution process. In the second method, they are a function of the type and amount of blowing agent and the foaming conditions.

¹ D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

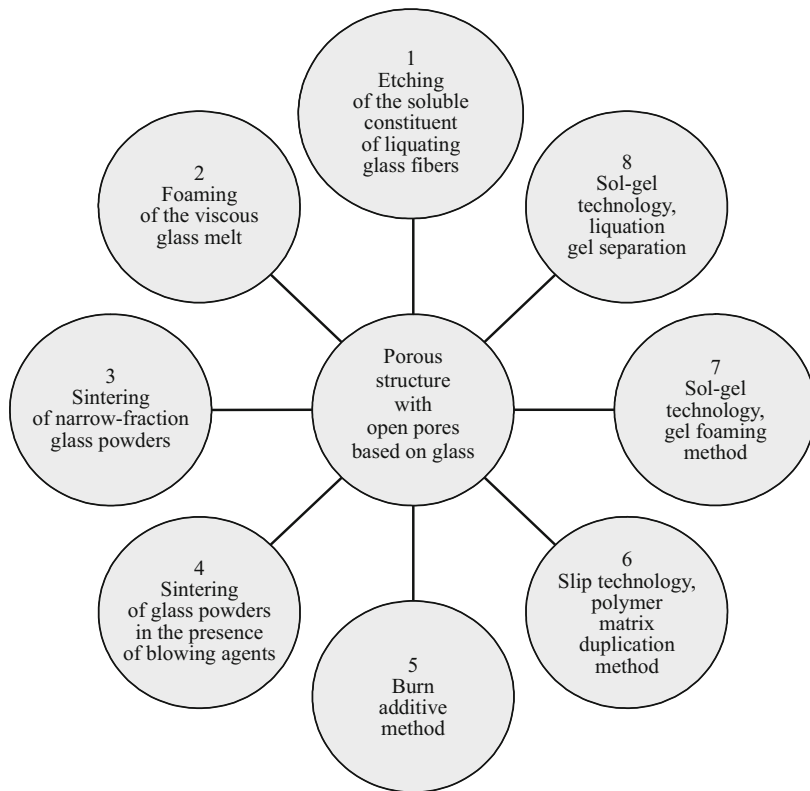


Fig. 1. Methods of manufacturing glass and glass-ceramic porous materials.

The etching method is thus laborious, multiparameter, and it is difficult to obtain large pores with the method so that it is virtually not used for fabrication of bioactive materials.

Cylinders with porosity at the 40% level, length of 6 and diameter of 4 mm were obtained by sintering of narrow-fraction calcium polyphosphate powders with a particle size of 45 – 105, 105 – 150, and 150 – 250 μm [3]. The pore size is a function of the size of the sintered fraction and does not exceed 100 μm . Use of “bundles” of these cylinders as implants allows obtaining an article with a bimodal pore structure. The pore space is composed of the channels between them and the porosity of the cylinders themselves. It is impossible to obtain materials with porosity greater than 50% with this method.

Different porous materials are made with blowing agents that totally or partially decompose at the sintering temperature and form a large amount of gas phase. The BAK-KS bioactive composite is obtained by sintering bulk-crystallizable silicon-doped calcium phosphate glass with a Ca : P atomic ratio of 0.8 : 1.0 and hydroxyapatite (HA) with CaCO_3 blowing agent, with 30 – 60% porosity and 15 – 30 MPa compressive strength (RF Patent No. 2053737). Porous glass with 70 – 200 μm pores is made from the following composition (mass content, %): 45.0 SiO_2 , 24.5 Na_2O , 24.5 CaO , and 6.0 P_2O_5 , melted at 1350°C. Blowing agents: 2 – 3% CaCO_3 or NaHCO_3 , are added to glass powder with a particle size of 40 – 70 μm and the mixture then undergoes

hot molding in a vacuum at a pressure of 50 MPa and temperature of 460°C for 2 h (US Patent No. 5676720). The use of a blowing agent is one of the most widely used manufacturing methods; its basic drawbacks include the complexity of obtaining structures with pores of the same size.

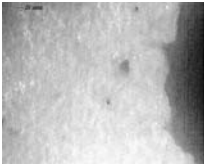
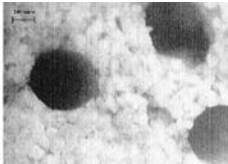
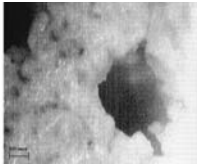
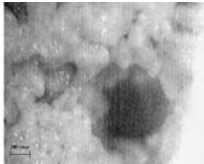
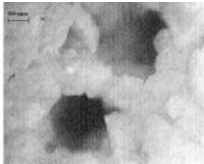
The burn additive method is based on using powders or granules of organic compounds as blowing agents and is essentially a variety of the previous method. The basic difference in the temperatures of burning organic substances is that it is much lower than the sintering temperature, but the amount of gas phase formed is large and the porosity of these materials is usually higher than when inorganic blowing agents are used. In addition, reaction between the burn additive and the glass at the sintering temperature is totally excluded. The sintered materials, whose porosity can vary from 30 to 70% (average macropore size of 360 μm and micropore size of 2 – 15 μm as a function of the polyvinyl butylene content, molding pressure, and sintering time) are obtained by mixing 0.093, 0.1 μm as a function of the polyvinyl butylene content, molding pressure, and sintering time) are obtained by mixing 0.093, 0.118, and 0.420 mm particles of polyvinyl butylene with HA powder in the ratio of 42 : 61 vol.% [4].

Burn additives can be incorporated in the stock for sintering while mixing the glass powder with a temporary process binder. In this case, when they are eliminated, pores are formed whose shape is more or less spherical. We tested graphite rods 0.5 – 0.7 mm in diameter placed in premolded stock made of calcium phosphate glass powder as burn additives. As a result of heat treatment of this stock, a structure with two types of pores was formed in the sintered calcium phosphate glass-ceramic material — channels from 540 μm in diameter and 30 – 140 μm round pores in the space between channels (see Table 1).

The basic merit of the polymer matrix duplication method is the possibility of obtaining a structure with 90 – 95% open porosity. The method consists of the stages of selecting the matrix, making up the slip, impregnating the matrix with it, drying the stock, and sintering the glass or ceramic base of the slip simultaneously with burning out the polymer matrix. The polymer foam matrix defines the structure of the porous material (pore size, number and method of their connection). Pores with a wide range of sizes are usually present in foam and the slip must fill both large and small pores equally well and form a homogeneously thick coating over the entire surface of the foam.

Slips with high fluidity and good adhesion to the polymer are used for impregnation. The powders for preparing this slip must be finely disperse with a small difference in the size form the average value and the binders and plasticizers

TABLE 1

Index	Cross section of sintered calcium phosphate glass-ceramic material ($\times 350$)				
					
Glass powder fraction, μm	40 – 80	80 – 125	125 – 250	250 – 315	315 – 400
Porosity, %	46	54	48	44	44
Channel diameter, μm	580	560	560	540	530
Pore size, μm	30	85	90	130	140

must not have components than could have a harmful effect on the human body.

The duplication method can be used to fabricate glass, glass-ceramic, and composite porous materials and when bioactive polymers and bioactive powders are used, the sintering stage is not mandatory. A composite material with a macroporous structure and a wide range of pore sizes (10 – 1000 μm) and bulk porosity of 70 – 95% can thus be obtained with crystalline calcium phosphates (HA, for example), bioglass (Bioglass and CP), polylactide acids (bioactive matrix), and titanium oxide (European Patent No. 9816267) or composite material based on glass powders of the system $\text{CaO} - \text{P}_2\text{O}_5 - \text{Na}_2\text{O} - \text{MgO}$ and porous α -tricalcium phosphate ceramic and highly porous polymer foam — a bioinert matrix (CPR Patent No. 1830907). A composite porous material 2.0 – 2.5 mm thick with 50 – 500 μm pores for plastic surger for bone defects was obtained from the bioactive polymer PLGA (polylactide glycol) and bioactive glass S53P4 (20 vol. %) [5].

Highly porous sintered glassy materials made from 45S5 Bioglass powder with a 5 μm particle size and polyurethane foam (bioinert matrix) by heat treatment at 900, 950, or 1000°C were obtained by the same method. The porosity of the initial polymer foam was 91%, the porosity of the sintered material was 70%, the average pore size was 510 – 720 μm , and the compressive strength was 0.3 – 0.5 MPa [6].

Another modification of the matrix duplication method is addition of a burn additive to the slip, which gives the final material additional porosity. A porous bioinert-bioactive composite ceramic material based on slip from HA and titanium powders and a polymer foam (bioinert matrix) was obtained by combining the burn additive and matrix duplication methods. The porosity level attained was $65 \pm 4\%$, the pore diameter was 100 – 1000 μm , Young's modulus was 1.7 ± 0.2 GPa, the bending strength was 2.1 ± 0.3 MPa, and the compressive strength was 7 ± 1 MPa [7].

We tested the technology with impregnation of No. 10 cotton thread with slip from calcium phosphate powder and a solution of polyvinyl alcohol as a variant of the matrix duplication method for obtaining channel pores. Bilayer materials

with a dense surface with maximum porosity of 20% and a highly porous internal layer with channels of regular shape over the entire length of the sample and an average diameter of approximately 130 μm were obtained with this method (Fig. 2).

The problem of obtaining structures that simulate the structure of natural bone is still pressing, since none of the listed methods (sintering of narrow-fraction powders, use of a burn additive, and slip impregnation of polymer foam) makes it possible to obtain porous structures that totally reproduce the heterogeneous structure of natural bone. The developmental trends in this direction are 3D modeling of bone fragments [8], creation of matrices that reproduce the model, and technology that allows obtaining porous material with an assigned structure. The sol-gel method and layer accretion laser technology are the most interesting and promising for reproducing such complex models with a multilevel gradient structure.

The patents and publications in the past five years indicate the possibility of using the sol-gel method for fabrication of porous bioglass. The structure is formed in the stage of gelation of a system that contains components responsible

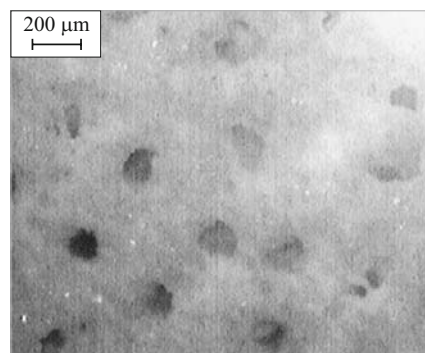


Fig. 2. Sintered calcium phosphate glass-ceramic material with channel pores (cross section, $\times 350$). Bilayer sample, burn base — filament, sintering temperature of 950°C; porous layer: number of channels, 130; channel diameter, 133 μm ; wall thickness, 290 μm ; dense layer thickness, 1500 μm .

for pore formation. Porous stock is obtained with a blowing agent that reacts with liberation of gas phase during foaming of gel corresponding to the following glass composition (molar content, %) at 600–900°C: 40–55 SiO₂, 15–25 CaO, 15–25 Na₂O, 1–9 P₂O₅. Further heat treatment at 1250–1600°C causes them to vitrify, and at temperatures of 500–700, 600–900, or 900–1200°C, produces materials with a different degree of crystallinity. The volume porosity of the materials attains 70%, while the pore size varies from 630 to 1250 μm (French Patent No. 2873683R).

Another method of obtaining porous materials with homogeneous pores uniformly distributed over the entire volume is based on the liquation properties of the gelating systems.

Porous bioactive glass is obtained by the sol-gel method in a pseudobinary system consisting of a mixture of organic and inorganic polymers. The organic polymer is the porous matrix, while the inorganic polymer is the bioactive glass. When a solution of the organic polymer is added to a gelating gel of the composition of bioactive glass, spinodal phase separation of the system takes place. Both polymer phases — inorganic and organic and uniformly distributed in each other — are formed at the equilibrium temperature, and each phase can liquefy in further heat treatment of the material. Removal of the polymer product results in a microstructure with communicating pores of the same diameter, which is a function of the process parameters. Initial separation of the polymer phase allows obtaining a more homogeneous pore structure [9].

The method of fabricating stock for sintering with construction of 3D models of a concrete bone fragment is used for fabricating implants with the required pore structure. Bioglass powder with a stoichiometric ratio of components of SiO₂ : CaO : P₂O₅ = 70 : 26 : 4, prepared by the sol-gel method, is then mixed with solutions of monomers to obtain a homogeneous paste and polymerized until a hard polyurethane foam is created and treated with heat at 1000°C for 10 h with holding at 600°C for 30 min to completely burn

out the foam. The materials obtained have 48–58% porosity and 50 to 200 μm pore size.

The inarguable merit of sol-gel technology is the existence of a wide assortment of precursors which allow forming the structure of a porous material at low temperatures in the stock fabrication stage. The drawbacks include the complexity of obtaining the macroporous materials required for colonization of bone cells. Nevertheless, the use of precision technologies will make it possible to predict the properties and structural types of materials obtained and move their parameters as close as possible to the characteristics of natural bone.

REFERENCES

1. I. Ya. Guzman, *Porous Ceramics* [in Russian], Moscow (2005).
2. K. Warden, *New Intellectual Materials and Structures* [in Russian], Tekhnosfera, Moscow (2006).
3. M. D. Gryn timer, R. M. Pilliar, R. A. Kandel, et al., "Porous calcium polyphosphate scaffolds for bone substitute applications *in vivo* studies," *Biomaterials*, **23**, 2063–2070 (2002).
4. Dean-Mo Liu, "Fabrication of hydroxyapatite ceramic with controlled porosity," *J. Mater. Sci.: Mater. Med.*, **8**, 227–232 (1997).
5. E. Orava, J. Korventausta, M. Rosenberg, et al., "In vitro degradation of porous poly(DL-lactide-co-glycoside) (PLGA) bioactive glass composite foams with a polar structure," *Polym. Degrad. Stability*, **92**, 14–20 (2007).
6. Q. Z. Chen, I. D. Thompson, and A. R. Boccaccini, "45S5 Bioglass-derived glass-ceramic scaffolds for bone tissue engineering," *Biomaterials*, **27**, 2414–2425 (2006).
7. E. Fidancevska, G. Ruseska, J. Bossert, et al., "Fabrication and characterization of porous bioceramic composites based on hydroxyapatite and titania," *Mater. Chem. Phys.*, **103**, 95–100 (2007).
8. J. R. Jones, O. Tsigkou, E. E. Coates, et al., "Extracellular matrix formation and mineralization on a phosphate-free porous bioactive glass scaffold using primary human osteoblast (HOB) cells," *Biomaterials*, **28**, 1653–1663 (2007).
9. C. M. Lofton, C. B. Milz, H. Huang, and W. M. Sigmund, "Bicontinuous porosity in ceramics utilizing polymer spinodal phase separation," *J. Eur. Ceram. Soc.*, **25**, 883–889 (2005).